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THE INFRARED ABSORPTION SPECTRA OF METAL OXIDES

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NASA TT F-11,483

Translation of an article from

Japan Analyst, V. 16, No. 10, pp. 1050-1055, 1967

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N68-15868 (ACCESSION NUMBER) (THRU) 1 (PAGES) 06 (CODE) (CATEGORY) (NASA CR OR TMX OR AD NUMBER) FACILITY FORM 602

GPO PRICE $ _____

CFSTI PRICE(S) $ _____

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 FEBRUARY 1968

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THE INFRARED ABSORPTION SPECTRA OF METAL OXIDES[1]

O. Kammori, N. Yamaguchi, K. Sato[2]

ABSTRACT: In order to apply an infrared spectrometry to the analysis of nonmetallic inclusion in steel, the identification of corrosion products and the study of surface treatment on steel plate, infrared absorption spectra of 25 kinds of metal oxides (α-Al_2O_3, CaO, CeO_2, Co_3O_4, CrO_3, Cr_2O_3, CuO, FeO, α-Fe_2O_3, Fe_3O_4, MgO, MnO, NiO, PbO, PbO_2, Sc_2O_3, α-SiO_2, SnO, SnO_2, TiO_2, V_2O_3, V_2O_5, Y_2O_3, ZnO and ZrO_2) were examined in detail. The spectra were measured by means of potassium bromide disk technique and nujol paste technique over the frequency region between 1400 and 400 cm^{-1}. Several of the oxides were also studied for their far infrared spectra between 400 and 60 cm^{-1}.

These oxides were found to have specific absorptions in the measured region, and showed definite correlations between their spectra and crystal structures.

(1) Oxides of iron, FeO, α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4, can be easily identified by comparison of their spectra.

(2) CrO_3, PbO, SnO and V_2O_3 give specific absorptions quite distinguishable from those, respectively, of Cr_2O_3, PbO_2, SnO_2 and V_2O_5.

(3) NaCl type oxides, MgO, CaO, FeO etc., have only one absorption at near 400 cm^{-1}, so that a force constant of M-O bond can be easily calculated as a diatomic molecule: e.g., that of ferric oxide, FeO, was 1.24 md/A.

(4) Spinnel ($MgAl_2O_4$) type oxides have coupling absorption at near 570 and 390 cm^{-1}.

(5) Silicon dioxide can be easily distinguished from the mixed sample of FeO, MnO, SiO_2, Cr_2O_3 and Al_2O_3, in the analysis of nonmetallic inclusion in steel. It was recognized, moreover, that the absorbance, $\log(I_0/I)$, and quantity SiO_2 were linearly correlated.

1. Introduction

Among the basic studies pertaining to steel and iron, those which relate /1050[3] to oxides are indispensible. Such studies are the object of investigations, particularly into inclusions in steel, corrosion, the preservation of steel and the surface treatment of steel plate. On the other hand, owing to the fact that infrared absorption methodology is effective for confirming the presence of

[1] Infrared Absorption Spectrum Studies of Iron and Steel (Report No. 1).

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[3] Numbers in the margin indicate pagination in the foreign text.

amorphous materials, which cannot be investigated through the use of x-ray diffraction and other techniques, the utilization of infrared absorption spectroscopy is anticipated in the future applied studies. On the basis of this reasoning, the writers selected 25 oxides whose presence in steel was assumed. These oxides were subjected to infrared spectroscopic absorption analysis.

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Infrared absorption spectrum data that have been accumulated in the past have been limited principally to a body of information involving the inorganic compounds. Some reports have appeared in general studies [1-3] and in books [4], but there is little literature concerning the oxides and what is abailable is only representative in nature. There are virtually no integrated studies of this subject. The subjects of physico-chemical treatment, particularly force constants and calculations of normal vibrations are virtually virtually untouched. We know of only a few qualitative studies of the oxides of divalent metals, such as those pertaining to silicon monoxide [5], [6] stannous oxide [6] [7], cerium monoxide [5], lead monoxide [5], selenium oxide [8], tellurium oxide [8], barium oxide, magnesium oxide [9] [11], zinc oxide, cupric oxide [12] and nickel oxide [13].

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In recent years many studies have been published on the subject of the infrared absorption of corrosion products. Prospects for the further development of this field are faborable, to cite the studies of Matsutaka [14] and Maekawa and Terade [15], for example. As a means of synthesizing data concerning the infrared absorption spectra of metal oxides, and as a means of leading into basic studies of these materials in iron (Fe) and steel, the authors have investigated the correlation between the absorption spectra and the crystal structure of 25 representative metal oxides as well as the possible application of this data to chemical analysis.

2. Experiments

2.1 Measurements

In applying the potassium bromide disk technique, 1 mg of the test samples was mixed with 300 mg of powdered potassium bromide. This was prepared in pellet form for the measurements. The potassium bromide powder used had been prepared by powdering simple crystals in a grinder mill and drying the powder in a vacuum at 120°C for several days. The normal methods were followed when the Nujol paste technique was used. For measurements in the extreme infrared spectra at 400 cm^{-1} (25 μ) or below, the kneaded polyethylene method was used.

Properly, the spectra should have been divided above and below 400 cm^{-1} for presentation, however, in order to permit comparisons, both of these ranges are shown in the same charts for the sake of convenience.

The equipment used was a Perkins-Elmer Model 521 Diffusion Grating Spectroscope and the FIS-1 and FIS-21 Type Hitachi Extreme Infrared Spectroscope used together. The measurement region was 60 -- 1,400 cm^{-1} (about 7 - 167 μ).

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2.2 Test Materials

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The materials tested are the 25 types of metal oxides given in Table 1. All of the samples were of commercial grade, confirmation of their properties was by x-ray diffraction.

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TABLE I. METAL OXIDE SAMPLES

No.	Sample	Purity	Identification†
1	Aluminum oxide, Al_2O_3	1st grade	α-Al_2O_3
2	Calcium oxide, CaO	〃	CaO
3	Ceric oxide, CeO_2	99.99%	CeO_2
4	Cobalt oxide, Co_3O_4	99.9%	Co_3O_4††
5	Chromium trioxide, CrO_3	Best purity	CrO_3††
6	Chromic oxide, Cr_2O_3	—	Cr_2O_3
7	Cupric oxide, CuO	—	CuO
8	Ferrous oxide, FeO	—	FeO
9	Ferric oxide, Fe_2O_3	Special grade	α-Fe_2O_3
10	Ferrosic oxide, Fe_3O_4	1st grade	Fe_3O_4
11	Magnesia, MgO	—	MgO
12	Manganese oxide, MnO	99.9%	MnO
13	Nickel oxide, NiO	99.9%	NiO
14	Lead monoxide, PbO	1st grade	PbO††
15	Lead dioxide, PbO_2	1st grade	PbO_2
16	Scandium oxide, Sc_2O_3	99.9%	Sc_2O_3
17	Quartz, SiO_2	1st grade	α-SiO_2
18	Stannous oxide, SnO	99% up	SnO
19	Stannic oxide, SnO_2	99% up	SnO_2
20	Titanium oxide, TiO_2	1st grade	TiO_2 (Anatase)
21	Vanadium sesquioxide, V_2O_3	99%	V_2O_3†††
22	Vanadium pentoxide, V_2O_5	99.9%	V_2O_5
23	Yttrium oxide, Y_2O_3	99.9%	Y_2O_3
24	Zinc oxide, ZnO	1st grade	ZnO
25	Zirconium oxide, ZrO_2	Special grade	ZrO_2

† Identified by means of X-ray diffraction method, †† Unknown material involved, ††† VO_2 and other unknown material involved

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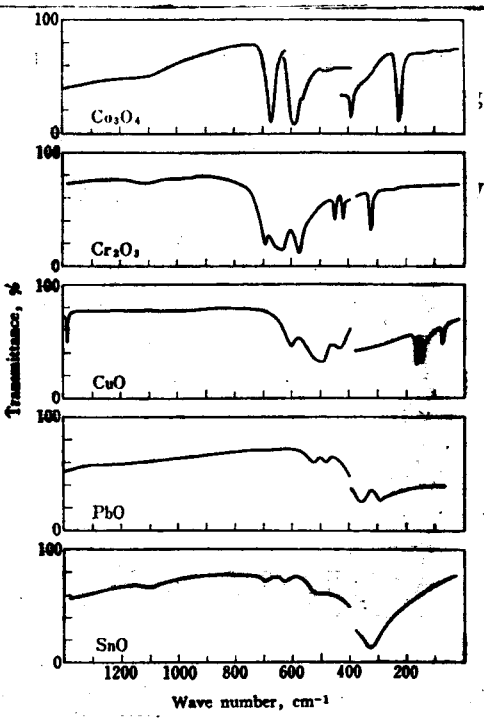

Figure 1. Infrared Absorption Spectra of Metal Oxides (Part I)

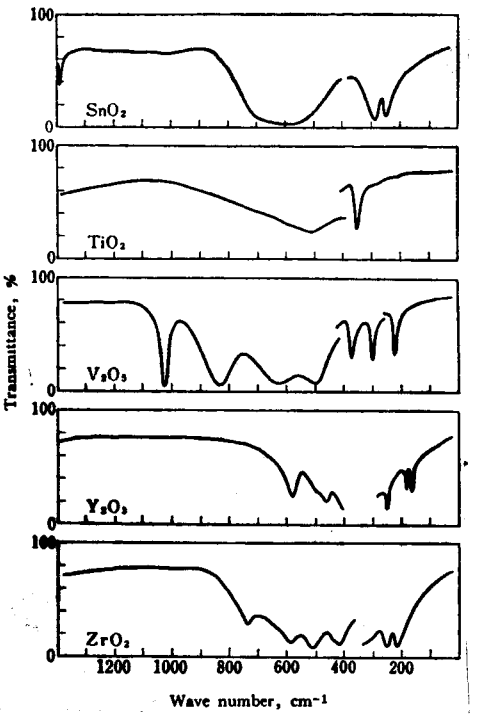

Figure 2. Infrared Absorption Spectra of Metal Oxides (Part II)

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3. Experimental Data

The infrared absorption spectra obtained for the 25 oxides are given in Figure 1 through 5. It was apparent that virtually all of the test samples exhibited characteristic absorption properties within the measured regions (400 -- 1,400 cm^{-1}). It was also noted that when 10 of the oxides were tested in the extreme infrared region of 60 -- 400 cm^{-1} (25-166 μ), they all demonstrated individual characteristic absorption properties. These 10 oxides were tricobalt tetroxide, chromium oxide, cupric oxide, zinc oxide, stannous oxide, stannous dioxide, titanium oxide, vanadium pentoxide, yttrium oxide, and zirconium oxide. Their characteristic absorption spectra are shown in consolidated form in Tables II and III.

The data given in Figures 1 through 5 and in Tables II and III are the wavelengths as obtained through the potassium bromide disk method. No major discrepancies were seen between the absorption positions obtained through the potassium bromide disk method and those obtained using the Nujol paste method.

4. Discussion

Characteristic absorption spectra were observed for all of these oxides,

except for an aberration in the vicinity of 400 cm^{-1} (25 μ thought to be attributable to vibrations of the grating. As is apparent in Tables II and III, the characteristic absorption positions do not overlap, and it is thought, that for this reason, they would be effective for use in qualitative analysis except where the absorption band is broad. There is, however, some difficulty in discriminating between the compounds whose crystalline structure [17] is similar, particularly those oxides of the divalent metals whose absorption spectra are broad and lie in the vicinity of 400 cm^{-1}. Mixed samples, in particular, have broad and overlapping absorption ranges making discrimination between their constituent materials difficult. In such cases, however, the extreme infrared region of 400 cm^{-1} or lower may be used to advantage. The information acquired through the studies is discussed below.

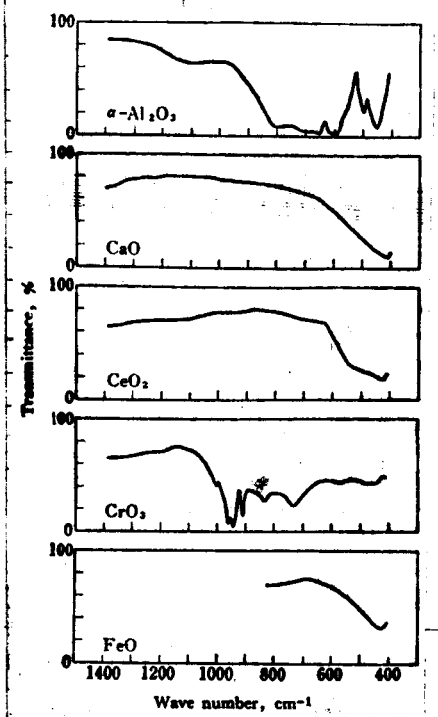

Figure 3. Infrared Absorption Spectra of Metal Oxide (Part III).

4.1 The Iron Oxides

The primary iron ores and corrosion products which have been subjected to analysis (4) are ferrous oxide, α-ferric oxide, γ-ferric oxide and triiron tetroxide. These materials are easily distinguishable because their infrared absorption spectra are in the high wavelength ranges above 400 cm^{-1}.

Further, according to Maekawa *et al* [15], there are recognizable differences in the spectroscopic absorption of α-ferric oxide and γ-ferric oxide within the 5-30 μ range. Additionally, Matsutaka [14] has made observations within the 50-400 cm^{-1} (25-200 μ) region. He has reported that the ranges are broad, but that absorption is low. Thus, infrared absorption spectroscopy is fully adequate for use in the study of steel if the characteristic absorption of the oxyacids (α-FeOOH, etc.) are utilized together with those of the iron oxides.

4.2 The Oxides of Chromium, Lead, Tin and Vanadium

All of these oxides were studied in two different samples in which the valence of the metal component differed. Owing to the fact that the coordination numbers were different, the crystalline structures also differed greatly. It is apparent that it is easy to discriminate between them, because they all have clearly different absorption characteristics. The absorption of chromium oxide at 448 and 419 cm^{-1} is peculiar, making this

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TABLE III Spectral Positions of Infrared Absorption Bands of Metal Oxides. (Part II)

	~1000 cm^{-1}	900 cm^{-1}	800 cm^{-1}	700 cm^{-1}	600 cm^{-1}	500 cm^{-1}	400 cm^{-1}
Aluminum oxide, α-Al_2O_3	—	—	—	760 (s)	636 (s)	595 (s)	492(m), 439(s)
Calcium oxide, CaO	—	—	—	—	—	—	400 (s)
Ceric oxide, CeO_2	—	—	—	—	—	—	~460 (m)†
Chromium trioxide, CrO_3	1005 (m)	960(s), 942(s), 908(m)	830 (w)	735 (m)	—	—	—
Ferrous oxide, FeO	—	—	—	—	—	—	410 (m)
Ferric oxide, α-Fe_2O_3	—	—	—	—	—	543 (s)	472 (m)
Ferrosic oxide, Fe_3O_4	—	—	—	—	—	580 (s)	—
Magnesium oxide, MgO	—	—	—	—	—	—	~480 (s)
Manganese oxide, MnO	—	—	—	—	—	—	440(s), 411(sh)
Nickel oxide, NiO	—	—	—	—	—	—	448 (m)
Lead dioxide, PbO_2	1388(w)	—	—	—	—	—	—
Scandium oxide, Sc_2O_3	—	—	—	—	630 (m)	~530 (sh)†	435 (s)
Silicon dioxide, α-SiO_2	1170(m), 1083(s)	—	—	799(m), 780(m)	697 (m)	511 (m)	460 (s)
Vanadium sesquioxide, V_2O_3	—	—	—	—	—	540 (w)†	—
Zinc oxide, ZnO	—	—	—	—	—	530 (s)	498(s), 440(s)

† These values were obtained by means of nujol paste method.

characteristic effective for use. It is also extremely interesting, looking at the vanadium oxides, that there is no clear absorption by vanadium trioxide, but, conversely, vanadium pentoxide has four high absorption positions. Chromium trioxide is quite unstable in the air. However, a spectrum was obtained and this is indicated in the graph. It is questionable, however, whether or not the data pertaining to this absorption are completely reliable.

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4.3 The Sodium Chloride Type Oxides

There is only one characteristic absorption at about 400 cm^{-1} (25 μ) for magnesium oxide, calcium oxide, ferrous oxide and so forth. These compounds are also quite simple in construction. The various physical constants for these materials are easy to calculate when they are considered as diatomic molecules. To give an example, in the case of ferrous oxide the characteristic absorption position is 410 cm^{-1}. Using this wavelength as a base, its force constant may be calculated at 1.24 md/A [16]. /1054

There are a large number of berthollide compounds in these types of oxides. The oxygen content is not fixed and as a result there are differences in their lattice constants. However, because they are of simple construction, it is believed that the physico-chemical analysis of the iron oxides, which until now have been virtually unknown, may well commence with these compounds.

4.4 The Spinel Group Oxides

Triiron tetroxide and tricobalt tetroxide are classified as spinel group (Mg-Al_2O_4) oxides. These types of oxide demonstrate common infrared spectroscopic absorption patterns. Beautifully coupled characteristic absorption is apparent in the 300-600 cm^{-1} region [18] [19].

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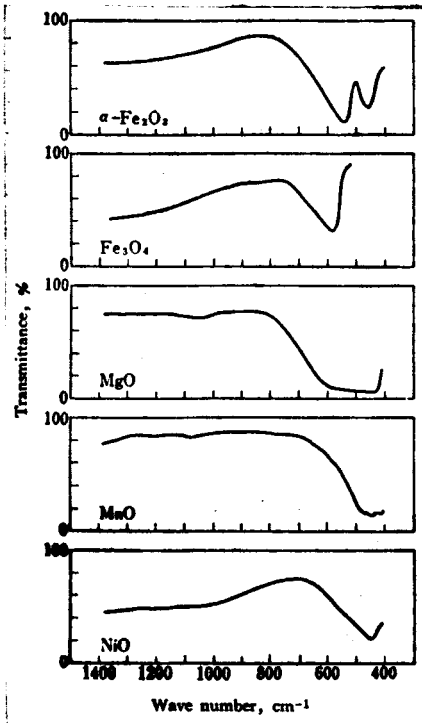

Figure 4. Infrared Apsorption Spectra of Metal Oxides (Part IV)

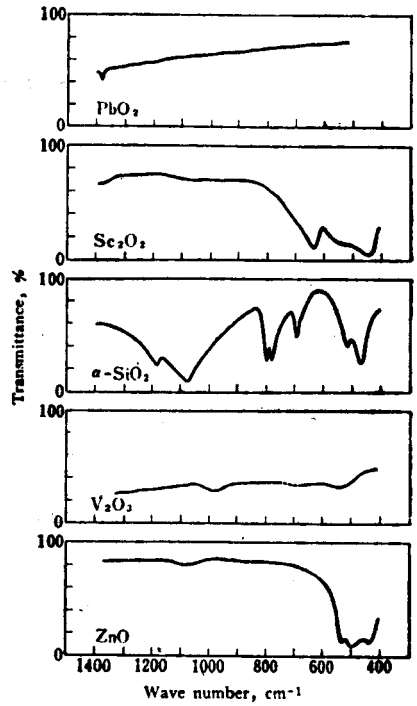

Figure 5. Infrared Absorption Spectra of Metal Oxides (Part V)

TABLE II Spectral Positions of Infrared Absorption Bands of Metal Oxides. (Part I)

	1400—700 cm⁻¹	600 cm⁻¹	500 cm⁻¹	400 cm⁻¹	300 cm⁻¹	200 cm⁻¹	200—60 cm⁻¹
Cobalt oxide, Co_3O_4	—	670 (s)	585 (s), 558 (sh)	—	390 (m)	218 (s)	—
Chromic oxide, Cr_2O_3	—	690 (s), 635 (s)	580 (s)	448 (m), 419 (m)	306 (m)	—	—
Cupric oxide, CuO	—	600 (m)	490 (m), 490 (m)	—	—	—	165 (m), 148 (m), 82 (m)
Lead monoxide, PbO	—	—	510 (w), 472 (w)	—	360 (w)	295 (w)	—
Stannous oxide, SnO	—	690 (w), 620 (w)	—	—	328 (m)	—	—
Stannic oxide, SnO_2	1400 (sh), 1385 (m)	600 (s)	—	—	—	295 (m), 252 (m)	—
Titanium oxide, TiO_2	—	—	500 (m)	—	355 (m)	—	—
Vanadium pentoxide, V_2O_5	1020 (s), 830 (s)	615 (s)	—	485 (s)	383 (m), 300 (m)	220 (m)	—
Yttrium oxide, Y_2O_3	—	—	560 (m)	460 (w)	—	240 (w)	182 (w), 172 (w)
Zirconium oxide, ZrO_2	726 (m)	—	581 (w), 510 (m)	425 (m)	—	256 (m), 225 (m)	—

Waldron [19] performed studies on a series of ferrites (MFe_2O_4: M = Co, Fe, Mg, Mn, Ni, Zn, etc.) Absorption in the vicinity of 570 cm^{-1} and 390 cm^{-1} was observed and he made a detailed analysis of this. In the present experiments triiron tetroxide and tricobalt tetroxide were taken as spinel type oxides. The absorption of tricobalt tetroxide was at 670 and 585 cm^{-1}. At both of these levels, a shift to higher wavelengths than Waldron's was observed, the difference in wavelength being 100 cm^{-1} and 200 cm^{-1}, respectively. Regardless of this, however, it is believed that both of these compounds provide typical examples demonstrating that infrared spectroscopic analysis of the spinel group oxides is possible.

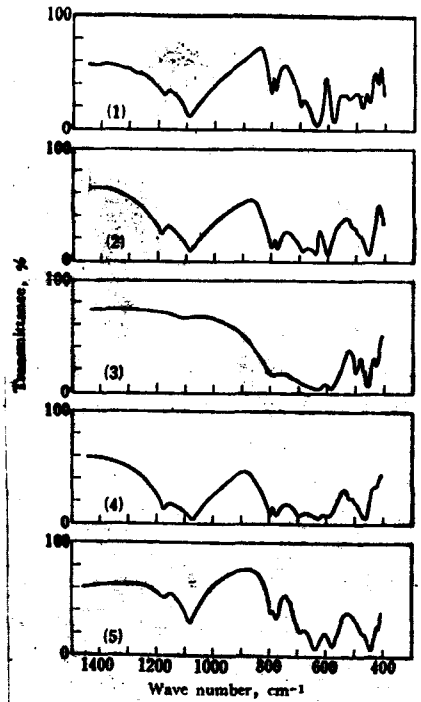

Figure 6. Infrared Absorption Spectra of Mixed Samples.

(1) SiO_2, Cr_2O_3; (2) SiO_2, Al_2O_3; (3) Cr_2O_3, Al_2O_3; (4) Cr_2O_3, Al_2O_3, SiO_2; (5) FeO, MnO, SiO_2, Cr_2O_3, Al_2O_3

4.5 The Spectra of Mixtures of Ferrous Oxide, Manganese Oxide, Silicon Dioxide, Chromium Oxide, and Alumina

These oxides constitute the primary inclusions found in steel and are the constant subjects of analysis. Ferrous oxide and manganese oxide may well be considered as being of the sodium chloride type, and it is found that their characteristic absorption closely resembles that of the latter. Chromium oxide and α-alumina are classified in the correndum group, however, some differences in the characteristic absorption of these compounds were observed. Silicon dioxide formed crystalline structures, independent of the other members of this group of five oxides.

The following discussion pertains to the results of tests which were made into the applicability of infrared spectra to quantitative analyses of these components when they were mixed together. Figure 5 gives the infrared absorption spectra for a mixed test sample made up of these five oxides (equal quantities with a total weight of about 1 mg).

Extremely interesting spectra were obtained. The following examples are given with respect to the question of differentiability.

1. Silicon dioxide could be distinguished from the other components quite easily, because its absorption spectrum is independent of the others.

2. It is difficult to distinguish between ferrous oxide and manganese oxide because the position of their characteristic absorption is

virtually identical.

3. If the effect of ferrous oxide and manganese oxide on chromium oxide is minimal, the latter can be identified by its relatively clear characteristic absorption at 448, and 419 cm^{-1}.

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4. Alumina can very easily affect the absorption of the other components. /1055

5. Accordingly, it is believed that only silicon dioxide can be isolated in a mixture containing these five different oxides and analyzed quantitatively.

It should be noted that the mixture which was examined here contained equal quantities of all of the components. Since, in actual practice, the included quantities would be different, it is believed that this method would be applicable to broad studies if suitable and effective methods can be devised.

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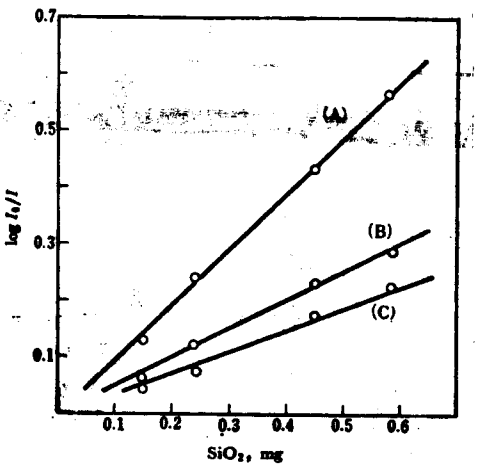

Figure 7. Calibration Curves of Silicon Dioxide.

(A) By the absorption at 1083 cm^{-1}, (B) By the absorption at 1170 cm^{-1}; (C) By the absorption at 780 cm^{-1}

These opinions are based on the study of the quantitative properties of silicon dioxide only. The material was prepared for study using the potassium bromide disk method. Ample care was taken by mixing the material in the mortar for the time necessary to assure uniformity. Figure 7 gives the content curve obtained using the base line method. It is apparent that good linearity was obtained.

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5. Conclusions

Studies were made of the infrared absorption spectra of metal oxides such as aluminum, calcium, etc. It has been pointed out that there is some correlation between the characteristic absorption and the crystalline formation of these substances. Finally, examples of the application of this method to analytical chemistry were presented and discussed. There have been similar fragmentary reports concerning the infrared absorption spectra of oxides, but no integrated studies have been found. It is planned to use the data presented here as a foundation for subsequent, detailed analytical chemical and physico-chemical studies of this subject.

In conclusion, warmest thanks are extended to the Chief of the Yawata Steel Co. Ltd., Tokyo Research Institute, Dr. Sanichiro Mizukawa, for his guidance and encouragement during the course of the present study, and to Mr. Toshiji Matsuhira of the Naga Plant of the Hitachi Manufacturing Co. Ltd., who conducted the extreme infrared absorption spectrum measurements.

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Translated for the National Aeronautics and Space Administration under Contract No. NASw-1695 by Techtran Corporation, PO Box 729, Glen Burnie, Md. 21061.

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